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<p>(21) International Application Number: PCT/IB98/01342 (22) International Filing Date: 28 August 1998 (28.08.98) (30) Priority Data: 97870141.5 19 September 1997 (19.09.97) EP (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): SCIALLA, Stefano [IT/IT]; Via F.B. Rastrelli, 81, I-00128 Rome (IT). BRIATORE, Andrea [IT/IT]; Via Riborgo, 16, I-17040 Savona (IT). DI CAPUA, Gloria [IT/IT]; Via Corona Boreale, 131, I-00040 Ardea (IT). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>
<p>(54) Title: USE OF PHOSPHONATE COMPOUNDS IN HYPOCHLORITE BLEACHING COMPOSITIONS</p>		
<p>(57) Abstract</p> <p>The present invention relates to the bleaching of textiles with hypochlorite bleaching compositions which comprise a phosphonate ingredient, for improved fabric whiteness and improved fabric safety.</p>		

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USE OF PHOSPHONATE COMPOUNDS IN HYPOCHLORITE BLEACHING COMPOSITIONS

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Field of the invention

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The present invention relates to the bleaching of textiles with hypochlorite bleaching compositions.

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Background of the invention

Bleaching compositions are well-known in the art. Amongst the different bleaching compositions available, those relying on bleaching by hypohalite bleaches such as hypochlorite are often preferred, mainly for performance reasons, especially at lower temperature.

However, a problem encountered with the use of hypochlorite based-compositions is the resulting damage and/or yellowing of the fabrics being bleached.

It is therefore an object of the invention to provide a hypohalite-containing composition, suitable for use in laundry applications, which provides improved fabric whiteness to fabrics treated therewith.

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It is another object of the invention to provide a hypohalite-containing composition, suitable for use in laundry applications, which provides improved fabric safety to fabrics treated therewith.

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The Applicant has thus now surprisingly found that this problem is solved by the provision, in a hypohalite bleaching composition, of a phosphonate

ingredient. Indeed, it has been found that improved fabric whiteness and/or safety were obtained with those composition, compared to hypohalite compositions without said phosphonate ingredient. The benefits are particularly noticeable in hypohalite bleaching compositions which further
5 comprise a pH buffering component.

Another advantage of the compositions in the invention is that they are chemically stable. By "chemically stable", it is meant that the hypohalite bleaching compositions of the present invention should not undergo more
10 than 15% loss of available chlorine after 5 days of storage at $50^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. The % loss of available chlorine may be measured using the method described, for instance, in "Analyses des Eaux et Extraits de Javel" by "La chambre syndicale nationale de L'eau de Javel et des produits connexes", pages 9-10 (1984). Said method consists in measuring the available
15 chlorine in the fresh compositions, i.e. just after they are made, and in the same compositions after 5 days at 50°C .

A further advantage of the compositions in the invention is that they are
20 suitable for the bleaching of different types of fabrics including natural fabrics (e.g., fabrics made of cotton, viscose, linen, silk and wool), synthetic fabrics such as those made of polymeric fibers of synthetic origin as well as those made of both natural and synthetic fibers. Indeed, the compositions in the present invention may be used on synthetic fibers despite a standing
25 prejudice against the use of hypohalite bleaches, especially hypochlorite bleaches, on synthetic fibers, as evidenced by warning on labels of commercially available hypochlorite bleaches and clothes.

EP 0 743 250 discloses a process producing bleaching compositions
30 comprising phosphonates. J07-109,107 discloses compositions comprising hypochlorite and a phosphonate ingredient. None of these prior art documents discloses the fabric whiteness and safety benefits obtained from the provision of a phosphonate ingredient in a hypochlorite composition.

The present invention encompasses the use, in a hypohalite bleaching composition, of a phosphonate ingredient, for providing improved fabric whiteness and/or safety to the fabrics treated therewith.

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Detailed description of the invention

According to the invention, there is provided the use, in a hypohalite bleaching composition, of a phosphonate ingredient for providing improved
10 whiteness and/or safety to the fabrics treated therewith. By "improved whiteness and/or safety", it is meant that hypohalite bleaching compositions, with the phosphonate ingredient, provide better whiteness, i.e. less yellowing, and/or fabric safety compared to hypohalite bleaching compositions which do not comprise said phosphonate ingredient. The
15 presence of a pH buffering component in the bleaching composition is not compulsory, but is highly preferred.

Hypohalite bleach

20 An essential component of the invention is a hypohalite bleach. Hypohalite bleaches may be provided by a variety of sources, including bleaches that are oxidative bleaches and subsequently lead to the formation of positive halide ions as well as bleaches that are organic based sources of halides such as chloroisocyanurates.

25

Suitable hypohalite bleaches for use herein include the alkali metal and alkaline earth metal hypochlorites, hypobromites, hypoiodites, chlorinated trisodium phosphate dodecahydrates, potassium and sodium
dichloroisocyanurates, potassium and sodium trichlorocyanurates, N-
30 chloroimides, N-chloroamides, N-chloroamines and chlorohydantoins.

For liquid compositions, the preferred hypohalite bleaches among the above described are the alkali metal and/or alkaline earth metal hypochlorites selected from the group consisting of sodium, potassium, magnesium,
35 lithium and calcium hypochlorites, and mixtures thereof, more preferably the alkali metal sodium hypochlorite.

For solid compositions, the preferred hypohalite bleaches among the above described are the alkali metal and/or alkaline earth metal hypochlorites selected from the group consisting of lithium hypochlorites, calcium hypochlorites, chlorinated trisodium phosphate dodecahydrates, potassium dichloroisocyanurates, sodium dichloroisocyanurates, potassium trichlorocyanurates, sodium trichlorocyanurates, and mixtures thereof, more preferably sodium dichloroisocyanurates and/or calcium hypochlorite.

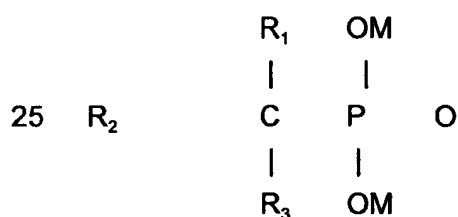
Preferably, the liquid compositions in the present invention comprise said hypohalite bleach such that the content of active halide in the composition is of from 0.1% to 20% by weight, more preferably from 2% to 8% by weight, most preferably from 3% to 6% by weight of the composition.

Preferably, the solid compositions in the present invention comprise said hypohalite bleach such that the content of active halide in the composition is of from 20% to 95% by weight, more preferably from 25% to 60% by weight of the composition.

Phosphonate ingredient

20

Suitable phosphonates for use herein are according to the formula :



- where M is H or an alkali metal;
- 30 - where R_1 , R_2 and R_3 independently are :
 - $-PO_3M_2$; or
 - $-H$; or
 - $-OH$; or
 - a hydrocarbon chain or cycle, optionally saturated, optionally substituted with one or several amino, oxy, amineoxy, phosphonic, sulphonic or alkoxy group, or mixtures thereof, said chain having of from 1 to 20 carbon atoms; or
- 35

- $\text{-NR}_4\text{R}_5$, where R_4 and R_5 independently are :
 - $\text{-PO}_3\text{M}_2$; or
 - -H ; or
 - -OH ; or
- 5 - a hydrocarbon chain or cycle, optionally saturated, optionally substituted with one or several amino, oxy, amineoxy, phosphonic, sulphonic or alkoxy group, or mixtures thereof, said chain having of from 1 to 20 carbon atoms.
- 10 Such phosphonates may include ethydrionic acid, hydroxy-ethane diphosphonic acid (HEDP) as well as aminophosphonate compounds, including amino alkylene poly (alkylene phosphonate), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates, diethylene triamine penta methylene
- 15 phosphonates and ethylenedinitrilotetrakis (methylenephosphonic acid) N,N-oxide. The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities.
- 20 Many of the suitable phosphonates suitable for use herein are aminophosphonates, while the amino group is somewhat unstable in a hypochlorite matrix. Accordingly stablized aminophosphonates are preferably used where the amino group is transformed into an N-oxide group, which in turn is stable to hypochlorite.
- 25 Preferred phosphonates for use herein are those produced by Monsanto under the tradename - Dequest® - and by Bozzetto under the tradename - Sequion® - and, among them, preferred are HEDP (hydroxy-ethane diphosphonate) and ATMP (amino trimethylenephosphonate) including their
- 30 N-oxidized version, and most preferred is ATMP N-oxide by Bozzetto (Sequion®CLR).
- 35 The phosphonate ingredients herein are present in amounts of from 0.001% to 20%, preferably 0.005% to 5%, most preferably 0.005% to 1% by weight of the total composition. Of course, mixtures of different phosphonate ingredients can be used.

The whitening effect, i.e. the yellowing-prevention effect, and /use of safety effect of the present invention can be evaluated by comparing the composition according to the present invention to the use of the same composition without the phosphonate ingredient.

5

The degree of yellowing can be determined by both visual and instrumental grading. Visually, the difference in yellowing between items treated with different compositions can be determined by a team of expert panellists. Instrumentally, the assessment can be determined with the help of

10 Colorimeters such as Ganz Griesser® instruments (e.g., Datacolor® Spectraflash® SF 500, Machbet White-eye® 500) or a ZEISS ELREPHO® or others which are available for instance from Hunterlab® or Gardner®.

Fabric safety may be evaluated by different test methods including the

15 degree of polymerisation test method according to UNI (Ente Nazionale Italiano di Unificazione) official method UNI 8282-Determinazione della viscosità intrinseca in soluzione di cuprietilendiammina (CED).

The compositions in the present invention are either in liquid or solid form.

20 Solid forms include forms such as powders, tablets and granules. Preferably, the compositions of the invention are in liquid aqueous form. More preferably, they comprise water in an amount of from 60% to 98% by weight, more preferably of from 80% to 97% and most preferably of from 85% to 97% by weight of the total aqueous liquid bleaching composition.

25

pH buffering component

A pH buffering component is an optional but highly preferred component for the compositions in the invention. The pH buffering component ensures that

30 the pH of the composition is buffered to a pH value ranging from 7.5 to 13, preferably from 8 to 12, more preferably from 8.5 to 11.5 after the composition has been diluted into 1 to 500 times its weight of water.

Suitable pH buffering components for use herein are selected from the

35 group consisting of alkali metal salts of carbonates, polycarbonates, sesquicarbonates, silicates, polysilicates, borates, metaborates, phosphates, stannates, alluminates and mixtures thereof, and preferably are

selected from the group consisting of sodium carbonate, sodium silicate, sodium borate, and mixtures thereof.

5 The raw materials involved in the preparation of hypohalite bleaches usually contain by-products, e.g calcium carbonate resulting in an amount of up to 0.4% by weight of by-product within the hypohalite composition. However, at such amount, the by-product will not have the buffering action defined above.

10 Liquid bleaching compositions herein will contain an amount of pH buffering component of from 0.5% to 9% by weight, preferably from 0.5% to 5% by weight, and more preferably in an amount of from 0.6% to 3% by weight of the composition.

15 Solid bleaching compositions herein will preferably contain an amount of pH buffering component of from 3% to 30% by weight, more preferably from 5% to 25% by weight, and most preferably in an amount of from 10% to 20% by weight of the composition.

20 pH

The pH of the liquid compositions in the present invention, as is, is typically from 12 to 14 measured at 25°C. Solid compositions or liquid compositions of the invention have a pH of from 7.5 to 13, preferably from 8 to 12, more
25 preferably from 8.5 to 11.5, when diluted into 1 to 500 times its weight of water. It is in this alkaline range that the optimum stability and performance of the hypohalite as well as fabric whiteness and/or safety are obtained. The pH range is suitably provided by the pH buffering component and the hypohalite bleach mentioned hereinbefore, which are alkalis. However, in
30 addition to these components, a strong source of alkalinity may also optionally be used.

Suitable sources of alkalinity are the caustic alkalis such as sodium hydroxide, potassium hydroxide and/or lithium hydroxide, and/or the alkali
35 metal oxides such as sodium and/or potassium oxide. A preferred strong source of alkalinity is a caustic alkali, more preferably sodium hydroxide and/or potassium hydroxide. Typical levels of such caustic alkalis, when

present, are of from 0.1% to 1.5% by weight, preferably from 0.5% to 1.5% by weight of the composition.

5 Optional polymers

An optional component of the compositions herein is a polymer. That polymer, has surprisingly been found to also reduce the yellowing of the fabrics treated therewith, i.e. improve whiteness, as well as improve fabric
10 safety. Naturally, for the purpose of the invention, the polymer has to be stable to the hypohalite bleach.

Suitable polymers for use are polymers comprising monomeric units selected from the group consisting of unsaturated carboxylic acids,
15 polycarboxylic acids, sulphonic acids, phosphonic acids and mixtures thereof. Co-polymerisation of the above monomeric units among them or with other co-monomers such as styrenesulfonic acid is also suitable.

Preferred examples of such polymers are the polymers and co-polymers of
20 monomeric units selected from the group consisting of acrylic acid, maleic acid, vinylsulphonic acid and mixtures thereof. Also suitable for use herein are the above mentioned polymers and co-polymers which are modified in order to contain other functional groups such as aminophosphonic and/or phosphonic units. More preferred polymers are selected from the group
25 consisting of polyacrylate polymers, co-polymers of acrylic and maleic acid, co-polymers of styrene sulphonic acid and maleic acid, and mixtures thereof, preferably modified with aminophosphonic and/or phosphonic groups.

The molecular weight for these polymers and co-polymers is preferably
30 below 100,000, most preferably between 500 and 50,000. Most suitable polymers and co-polymers for use herein will be soluble in an amount up to 0.1% by weight, in an aqueous composition comprising 5% by weight of sodium hypochlorite with its pH adjusted to 13 with sodium hydroxide.

35 Commercially available such polymers, suitable for use herein, are the polyacrylate polymers sold under the tradename Good-Rite® from BF Goodrich, Acrysol® from Rohm & Haas, Sokalan® from BASF, Norasol®

from Norso Haas. Also suitable for use herein are the co-polymers of styrene sulphonic acid and maleic acid, commercially available under the tradename Versaflex® from National Starch such as Versaflex 157, as well as Acumer® terpolymers from Rohm and Haas, in particular Acumer® 3100.

- 5 Preferred commercially available polymers are the polyacrylate polymers, especially the Norasol® polyacrylate polymers and more preferred are the polyacrylate polymer Norasol® 410N (MW 10,000) and the polyacrylate polymer modified with phosphonic groups Norasol® 440N (MW 4000) and its corresponding acid form Norasol® QR 784 (MW 4000).

10

A preferred polymer for use herein is a polyacrylate polymer modified with phosphonic groups commercially available under the tradename Norasol® 440N (MW 4000) and its corresponding acid form Norasol® QR 784 (MW 4000) from Norso-Haas.

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Mixtures of polymers as herein described may also be used in the present invention.

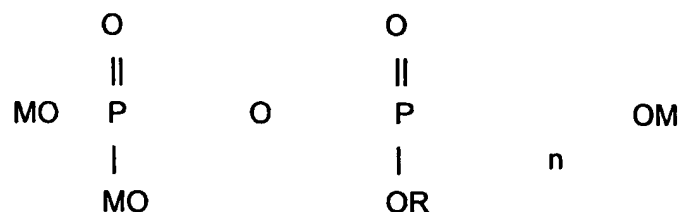
- 20 Polymers herein are preferably present in low amounts, i.e. in amounts of up to 0.5% by weight, more preferably from 0.001% to 0.3% by weight, most preferably from 0.005% to 0.2% by weight of the liquid composition.

Optional phosphates

- 25 An optional component of the compositions herein is a phosphate. That phosphate has surprisingly been found to also reduce the yellowing of the fabrics treated therewith, i.e. improve whiteness, as well as improve fabric safety. Suitable phosphates for use herein are :

- linear or branched polyphosphates of structure

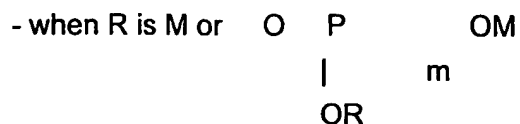
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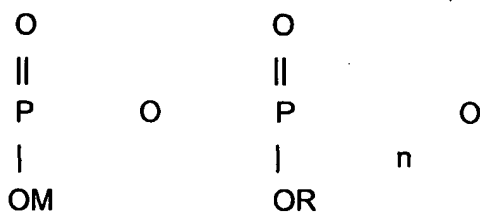
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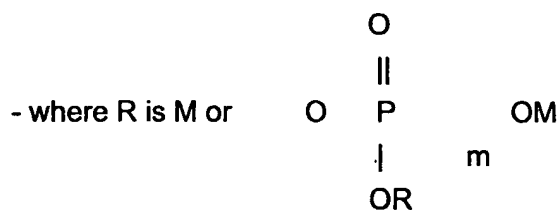
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- when M is a counterion, preferably alkali metal;
 - when $0 \leq n+m < 500$ (if $n+m = 0$ then the compound is phosphonic acid)

- cyclic polyphosphates (also referred to as metaphosphates), of structure

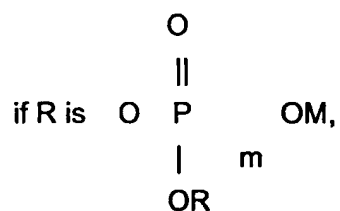
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the phosphate compound contains both cycles and branched chain, and can be referred to as an ultraphosphate.)

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- where M is a counterion, preferably an alkali metal
- where $0 \leq n+m < 500$

All such phosphate ingredients are suitable for use herein, and preferred are linear phosphate ingredients (i.e. R is M) where n is 1 (pyrophosphate) and n is 2 (tripolyphosphate), most preferably where n is 2. The most commonly available form of these phosphate is where M is Sodium.

35

The phosphate ingredients herein can be present herein in amounts of from 0.001% to 20%, preferably 0.005% to 5%, most preferably 0.005% to 1% by weight of the total composition. Of course, mixtures of different phosphate
5 ingredients can be used.

The composition in the invention may also comprise further optional components such as perfumes, bleach-stable surfactants, organic or inorganic alkalis, pigments, dyes, optical brighteners, solvents, chelating
10 agents, radical scavengers and mixtures thereof.

Preferably, the compositions in the invention are used in diluted form in laundry applications. The expression "used in diluted form" herein includes dilution by the user, which occurs for instance in hand laundry applications,
15 as well as dilution by other means, such as in a washing machine. Preferably, the composition is diluted into 5 to 500 times its weight of water for hand laundry application and 10 to 500 times its weight of water in a washing machine.

The invention is illustrated in the following non-limiting examples, in which all percentages are on a weight basis unless otherwise stated.

5

Examples

Composition (weight %)	1	2	3	4	5
Sodium hypochlorite	5.0	5.0	3.5	3.5	5
Sodium hydroxide	1	1.5	1	1.5	0.8
Sodium carbonate	1	2	2	1.5	2
Sodium silicate	-	-	0.5	0.5	0.5
Sodium metaborate	1	-	-	-	-
Sequion® CLR (N-oxydized aminotrimethylenephosphonate)	0.1	0.1	0.1	0.1	0.1
HEDP (Hydroxyethane diphosphonic acid)	-	-	-	-	-
STTP	-	-	-	-	-
Norasol 440N	-	-	-	-	-
Water and minors	up to 100%				

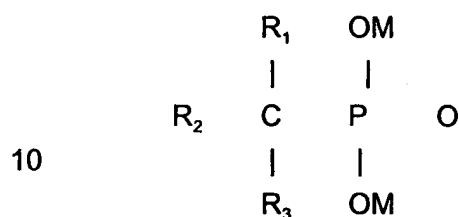
Composition (weight %)	6	7	8	9	10
Sodium hypochlorite	5.0	5.0	3.5	3.5	5
Sodium hydroxide	1	1.5	1	1.5	0.8
Sodium carbonate	1	2	2	1.5	2
Sodium silicate	-	-	0.5	0.5	0.5
Sodium metaborate	1	-	-	-	-
Sequion® CLR (N-oxydized aminotrimethylenephosphonate)	0.05	0.1	0.05	0.1	0.1
HEDP (Hydroxyethane diphosphonic acid)	0.05	0.02	-	-	-
STTP	0.05	-0	0.05	-	0.02
Norasol 440N	0.05	-	-	0.05	0.02
Water and minors	up to 100%				

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WHAT IS CLAIMED IS:

- 1- The use, in a hypohalite bleaching composition, of a phosphonate ingredient, for providing improved whiteness and/or safety to the fabrics treated therewith.
- 2- The use according to claim 1 wherein said composition further comprises a pH buffering component.
- 3- The use according to claim 2, wherein said pH buffering component is selected from the group consisting of alkali metal salts of carbonates, polycarbonates, sesquicarbonates, silicates, polysilicates, borates, metaborates, phosphates, stannates, alluminates, and mixtures thereof.
- 4- The use according to claim 3, wherein said pH buffering component is selected from the group consisting of sodium carbonate, sodium silicates, sodium borate, and mixtures thereof.
- 5- The use according to claims 2-4, wherein said pH buffering component is in an amount of from 0.5% to 9% by weight, preferably 0.5% to 5% by weight of the liquid composition or in an amount of from 3% to 30% by weight, preferably from 5% to 25% by weight of the solid composition.
- 6- The use according to any one of claims 1-5, wherein said hypohalite bleach is, for liquid bleaching compositions, an alkali metal sodium hypochlorite or, for solid compositions, sodium dichloroisocyanurate and/or calcium hypochlorite.
- 7- The use according to any one of claims 1-6, wherein said hypohalite, based on active halide, is present in an amount of from 0.1% to 20% by weight, preferably from 2% to 8% by weight of the liquid composition or in an amount of from 20% to 95% by weight, preferably from 25% to 60% by weight of the solid composition.

- 8- The use according to any one of claims 1-7, wherein said composition further comprises a strong source of alkalinity.
- 9- The use according to any one of claims 1-8, wherein said phosphonate ingredient is of structure :



- where M is H or an alkali metal;
 - where R_1 , R_2 and R_3 independently are :
 - $-PO_3M_2$; or
 - H; or
 - OH; or
 - a hydrogen chain or cycle, optionally saturated, optionally substituted with one or several amino, oxy, amineoxy, phosphonic, sulphonic or alkoxy group, or mixtures thereof, said chain having from 1 to 20 carbon atoms; or
 - $-NR_4R_5$, where R_4 and R_5 independently are :
 - $-PO_3M_2$; or
 - H; or
 - OH; or
 - a hydrocarbon chain or cycle, optionally saturated, optionally substituted with one or several amino, oxy, amineoxy, phosphonic, sulphonic or alkoxy group, or mixtures thereof, said chain having of from 1 to 20 carbon atoms.
- 10- The use according to any of the preceding claims, wherein said composition comprises from 0.001% to 20%, preferably from 0.005% to 5%, most preferably from 0.01% to 1% of said phosphonate ingredient.
- 11- The use according to any of the preceding claims, wherein said composition further comprises a polymer.

- 12- The use according to any of the preceding claims wherein said composition further comprises a phosphate.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 98/01342

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/395 C11D3/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 743 280 A (THE PROCTER & GAMBLE CO.) 20 November 1996 see the whole document ---	1-10, 12
Y	US 3 297 578 A (CRUTCHFIELD M.M. ET AL.) 10 January 1967 see the whole document ---	1-10, 12
Y	US 3 629 124 A (KING THOMAS M.) 21 December 1971 see the whole document ---	1-10, 12
A	EP 0 743 279 A (THE PROCTER & GAMBLE CO.) 20 November 1996 see claims 1,6-9 ---	1-8
A	EP 0 668 345 A (THE PROCTER & GAMBLE CO.) 23 August 1995 ---	1-8
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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In .ational Application No

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